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Review on micro-direct methanol fuel cells

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A B S T R A C T

Fuel cells have unique technological attributes: efficiency, minimization of moving parts and low emissions. The Direct Methanol Fuel Cell (DMFC) has attracted much attention due to its potential applications as a power source for transportation and portable electronic devices. With the advance of micromachining technologies, miniaturization of power sources became one of the trends of evolution of research in this area. Based on the advantages of the scaling laws, miniaturization promises higher efficiency and performance of power generating devices, so, MicroDMFC is an emergent technology. There has been a growing interest in the development of this type of micro cells in the last years, resulting both in experimental studies (operating conditions, cell design and new materials) and in modeling studies. Despite the increase in the knowledge acquired, many challenges are still to be reached. This paper provides a detailed comprehensive review both on fundamental and technological aspects of micro-direct methanol fuel cells. Special attention is devoted to systematization of published results on experimental area since to date and also to a special section dedicated to modeling studies.

Contents

1. Introduction

Nowadays, consumers demand for portable, power-hungry devices (3G-cellular phones, laptop computers and internet-enabled PDAs) has stimulated researchers and industry to develop

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advanced miniaturized portable fuel cells to overcome systematic limitations of conventional batteries [1–4]. Medicine is also a demanding field for miniature fuel cells as implantable micro-power sources [5]. Micro-fuel cells can compete with batteries in the low power range (0–30 W). The Proton exchange membrane (PEM) fuel cell and in particular the Direct methanol fuel cell (DMFC) have potential to meet these requirements. Mostly due to the lack of effective miniaturized hydrogen storage technologies, a liquid fuel like methanol is the best option to achieve a high power density with an attractive cost-to-power ratio. MicroDMFCs can operate at room temperature reducing the thermal management challenges for small systems. Small DMFCs with various degrees of microfabrication have been reported [6]. Recently, several companies such as Toshiba, Hitachi, Fujitzu, Samsung and IBM have registered significant developments on DMFC's for portable applications.

The central part of the MicroDMFC is the proton exchange membrane. Methanol crossover is one of the most important problems to solve. High methanol concentration provides achievable energy density but it also causes severe methanol crossover through the membrane resulting in a mix potential at the cathode, lowering cell performance. Concerning the different concepts of fuel delivery and handling, the MicroFCs are categorized as passive and active [7]. An active system needs moving parts to feed oxidant or fuel to the cell requiring power to operate. A passive system requires no external power (no need of auxiliary liquid pumps and gas blower/compressor) relying on diffusion and natural convection to deliver the fuel and oxygen. There are also cells that need a dispositive to supply the fuel but are passive at the cathode side, i.e., working in air-breathing operation. Most of the works on MicroFCs rely on active systems but there is an increasing interest in the passive cells exhibiting higher volumetric energy density and more design flexibility mainly when miniaturization is needed.

The channel design determines the flow distribution in MicroFCs. Cha [8] used numerical simulation to compare the performance of several designs. The design optimization demands for a better understanding of the flow dynamics. The control of the multiphase flows at the micro scale is a crucial issue. The CO_2 bubbles formed at the anode can disturb and, eventually, block the flow. Understanding how the drops affect the flow resistance in the cathode channels is essential to develop air breathing operation. On the cathode side the water produced is injected into the channels in active systems and the developed two-phase flow plays a central role in fuel cell water management [9]. The channels must be designed for low pressure drop to avoid excessive parasitic power losses and must operate in a regime adequate to maintain a proper overall water balance. Despite the importance of water management in determining the MicroFC performance, no detailed design optimization has been reported. Numerical simulation [7,9–12] works help the optimization of MicroDMFCs.

In the last years advances have been made in the MicroDMFC research and some review papers on this type of fuel cell are available, each one focusing on different aspects of this type of cells. Morse et al. published a review [13] that presents a discussion of micro-fuel cell technologies, providing insight into the innovations that have been made until 2007. Nguyen et al. [14] reviewed recent progress of the development of micro machined membrane fuel cells (MicroPEMFC and MicroDMFC). This review first discusses the scaling law applied to this type of fuel cell. Kundu et al. [5] discussed the status on the research and development of micro-fuel cell, namely Micro-reformed hydrogen fuel cell, hydrogen fed micro-fuel cell, MicroDMFC and Micro-direct formic acid fuel cell and their commercialization status were also reported. The different substrate materials used in micro-fuel cells for the suitability of the portable electronics have also been stated. The design aspects of micro-fuel cells and micro-reformers were also discussed. Kamarudin et al. [6] presented a review that discusses the challenges and development of MicroDMFC. Besides that, the paper also shows some marketing prediction in term of economics view. The most recent review [15] from Sundarrajan et al. focused only on micro-direct methanol fuel cells is a quite detailed review on the experimental field, although there is a lack of information on modeling area.

In this paper the most recent work done on Micro-methanol fuel cells has been reviewed. Design considerations (i.e. carrier subtract, proton exchange membrane, cell design, fuel and oxidant delivery system and flowfield effect) for MicroDMFC are presented. Operating conditions used in the works reviewed are summarized and the effect of each one on fuel cell performance is discussed. The performance of the MicroDMFC reviewed are compared and discussed. The main innovations are described in a separate section. Special emphasis is devoted to the modeling studies, since there is a lack of review information on this topic.

2. Design considerations

2.1. Carrier substrate

Two approaches are normally followed when designing fuel cells: scaling down of fuel cell system using conventional assembling methods or redesign every component using microelectromechanical system (MEMS) technology. With the conventional method a fuel cell is fabricated by hot-pressing the sandwich structure of gas diffusion layer, electrodes and electrolyte membrane. For MEM systems, silicon has been widely used as the carrier substrate. These MEMS enables notably mass fabrication at low cost (very large number of devices on a very small area), which could lead to a reduction in the global cost of miniature fuel cells [16]. The most common used silicon-based micromachining techniques are [14] deep reactive ion etching (DRIE), deposition of various materials using chemical vapor deposition (CVD) and physical vapor deposition (PVD). These techniques enable miniaturization of the fuel/oxidant delivery system and the deposition of electrodes and electrode materials. Stainless steel is another

Table 1
Comparison between the various types of substrates/fabrication techniques used on micro-methanol fuel cells.

Type of substrate	Fabrication techniques	Advantages	Disadvantages
Silicon	DRIE, CVD and PVD	High temperature resistance, facilitate the possible integration of the FCs with other electronic devices on the same chip	Fragility of silicon leads to difficulties in compressing the cell for good packaging, high cell contact resistance, low conductivity
Stainless steel	Etching, laser machining or punching	High conductivity and high mechanical strength	High cost for machining, possibility of corrosion
Polymers	Polymeric surface micromachining, hot embossing, soft lithography and laser machining	Good chemical stability, light weight and low cost	Low power density obtained and major possibility of leakages between substrate and membrane

material used, this substrate can be machined by etching, laser machining or punching.

Polymers are also attractive materials for MicroFCs due to the recent developments in polymeric micromachining. New techniques such as polymeric surface micromachining, hot embossing, soft lithography and laser machining are available [17]. Polymers like polymethylmethacrylate (PMMA), polydimethylsiloxane (PDMS) and SU-8 can be used as carrier substrate.

The different types of carrier substrates as well as the different microfabrication techniques with advantages and disadvantages are summarized on Table 1.

A significant amount of work using silicon as carrier substrate is available, recurring to different techniques to prepare the microchannels [18–29]. The study provided by Kamitani et al. [18] refers the use of microsystems techniques like DRIE and spin-coating to prepare the microfuidic and gas microchannels on silicon. Thermal oxide and LPCVD Si_3N_4 were deposited on both sides of the silicon wafer as the mask [19–21]. Double side lithography technology was introduced to form complicated flow structures of anode and cathode plates. In these works, the maximum power output achieved varies between 4.2 and 12.54 mW/cm^2. The flow fields designs presented by [22–28] are fabricated on silicon wafers by MEMS technology. Metal thin films were deposited on the surfaces of silicon wafers as current collectors. Power outputs between 10 and 34.2 mW/cm^2 were obtained. Meng et al. [29] fabricated microchannels by DRIE of a silicon wafer, followed by metal evaporation. In this work, better performances were obtained with methanol concentration 2 M and were around 17 mW/cm^2.

Stainless steel was also used in several works [30–34]. The flow field referred in Refs. [30–33] was made in stainless steel in order to enhance the conductivity and mechanical strength of the current collectors. The flow field is machined on a stainless steel plate by micro-stamping process. This technique is highly effective, easy to operate and low-cost. In order to repair the cracks existing after the fabrication process, a titanium layer was deposited onto the surface of each collector by the magnetron ion plating (MSIP) technology. Regarding the manufacture of the flow fields, Ghayor et al. [34] made copper EDM electrodes by wire cut machining and then produced cross strip flow field by using of electro discharge machining with copper electrode on stainless steel. Surface quality and channels dimensions accuracy was referred as acceptable. For stainless steel based flowfields, in the works reported, the maximum power output varies between 24.75 and 170 mW/cm^2.

As said before, polymers can also be used as carrier substrate [35–43]. Hashim et al. [35] reported a study on a single cell and a stack. To build up the flow channels, a PMMA plate was cut into small pieces with a specific size required using a CO_2 laser cutter. Then, a CNC Mazak machine was used to carve passing pattern for cathode and anode (methanol storage reservoir) on the small PMMA pieces. These pieces of PMMA were shaped to get anode and cathode plate with the pattern depth of 1.5 mm for reservoir. The highest power achieved was 12.05 mW/cm^2. The total cost for the MicroDMFC in this study is only about 2 USD/mW.

PDMS was chosen by Shen et al. [36] as material for the channels design because of its easy application and its good chemical resistance. In this work, a planar fuel cell (see Section 2.3) was designed based on three components: a PDMS chip with patterned microchannels, a narrow Nafion strip and a float glass substrate with catalytic electrodes. A maximum power density of 3.0 mW/cm^2 was obtained.

A concept for a flexible direct methanol micro-fuel cell, based on the micro structuring of a Cr/Au metalized, thin polymer film of photosensitive SU-8 was presented by Weinmueller et al. [37]. A combination of standard microfabrication/MEMS techniques with secondary modifications based on photolithography was applied to manufacture micro-sized flow fields in silicon and SU-8 films. In comparison to the rigid substrate based micro-fuel cells from the literature [38,39] the presented MicroDMFC concept can achieve reasonably high power densities of up to 20 mW/cm^2 even under bending conditions.

Esquivel et al. [40] also designed the fuel cell with current collectors consisting in two metalized SU-8 plates. The referred work exploits the capability of SU-8 components to bond to each other by a hot-pressing process and obtain a compact device. The components were first tested using an external casing obtaining a power output of 4.15 mW/cm^2. The components were then bonded to obtain a compact micro-direct methanol fuel cell that yielded a low power density of 0.65 mW/cm^2 under the same conditions. Despite this decrease in power density after bonding, the drastic reduction of the device dimensions resulted in an increase of more than 50 times the previous volumetric power density. The results obtained validate this novel approach to an all-polymer micro-fuel cell.

The channels of a planar cell (see Section 2.3) were mechanically eroded on a polycarbonate substrate with a numerical control device in the work reported by D'Urso et al. [41]. Polycarbonate was chosen because of its low weight, low cost and excellent insulating characteristics. A thin gold layer was deposited by sputtering, using a mask to prevent the deposition in the middle part of the cell, between the anodic and the cathodic channels. A maximum power density of 1.3 mW/cm^2 was obtained. Shen et al. [42] made by rapid power blasting the flow field of another planar cell. In this method, a SU-8 mold by lithography was used to put PDMS on a glass substrate. The PDMS forms a high-resolution powder blasting erosion-resistant mask, which is complementary to the SU-8. Next, using powder blasting, two microchannels are eroded. The PDMS layer was removed and a chromium adhesion layer followed by a gold layer was evaporated. The catalyst was then deposited (Pt/Ru at the anode side and Pt at the cathode side). Afterwards, by using stamping technology, a thin liquid PDMS layer was transferred onto the glass ship to form an adhesive layer. Finally, a Nafion membrane was mechanically clamped to the glass chip. This prototype could achieve an output power of 0.5 mW/cm^2.

Sun et al. [43] fabricated the channels in Acrylonitrile butadiene styrene (ABS) by double side hot embossing. The bipolar plates were metalized by several chemical and electrochemical steps and produced using hot embossing, a low cost, highly accurate batch process. A single cell was assembled to verify the self-pumping function, and it can generate a peak power density of 7.4 mW/cm^2.

The influence of the current collector materials (i.e., silicon, stainless steel and PMMA) on cell performance was simulated by Zhang et al. [30] using a two-dimensional mathematical model. Because of the excellent heat transfer qualities of silicon and stainless steel, uniform temperature distributions were achieved in the studied cells. The temperature difference between anode and cathode was much larger in the PMMA-based cell. Thus, considering the necessity of heating or dissipating heat in cells under certain conditions, silicon and stainless steel appear to be more suitable as current collector materials. From this work, it is obvious that the cell with stainless steel current collectors performed much better than the others. For the purpose of verifying the accuracy of the simulation results, the authors tested a metallic MicroDMFC with the operating parameters remaining constant and the testing results were compared to the data from the previous works of the same authors [44,45]. Effectively, the metallic cell generated the highest power densities (115 mW/cm^2 at 80 °C). This result demonstrated the superiority of stainless steel as the current collector material. Compared to metal current

collectors, the low electronic conductivity of silicon current collectors leads to a non-uniform current distribution, which is disadvantageous for reactant and catalyst utilization. In addition, the fragility of silicon leads to difficulties in compressing the cell for good packaging. Hence, the contact resistance in the cell is comparatively high. Although, possessing low electronic conductivity and thermal conductivity, the polymer is still a promising option for the current collector material because of its good chemical stability, light weight and low cost.

The most common materials used as carrier substrate are silicon and stainless steel. Generally, stainless steel leads to higher fuel cell performances. Some polymers have also been tested, but fuel cell performances are still lower than the acceptable. SU-8 seems to be the most promising polymer carrier substrate.

2.2. Membrane electrode assembly (MEA)

The central part of a fuel cell is the membrane electrode assembly that includes the catalytic layers, diffusion layers and the proton exchange membrane. The most important component is the polymer electrolyte membrane which must have relatively high proton conductivity, must be a barrier to the mixing of fuel and reactant gases and must be chemically and mechanically stable in the fuel cell environment. Typically, the membranes for MicroDMFC are made of perfluorocarbon-sulfonic acid ionomer which results from the combination of tetrafluorethylene with perfluorosulfonate monomers. The perfluorinated sulfonic acid membranes were developed by DuPont and sold under the commercial name of Nafion. Methanol crossover is one of the major problems regarding micro-methanol fuel cells technology. A part of the methanol does not react at the anode side and cross the membrane leading to a decrease on fuel cell performance. Methanol crossover can be reduced modifying some properties of the MEA, namely impregnating the Nafion membrane with Pd. There are also some works referring membranes based in other polymers [6].

The most common used catalysts in DMFCs are Pt/Ru on the anode side and Pt on the cathode side being the very high cost of these materials a major obstacle to commercialization. The microstructure of the catalyst layer is very important for the kinetics of the electrochemical reactions and for the species diffusion. A good interaction between the support and the catalyst improve catalyst efficiency and decrease catalyst loss and also govern charge mass transfer. The support can also assist in sufficiently enhancing the catalyst performance and durability by reducing catalyst poisoning. Accordingly to Sharma et al. [46] the choice of support material is vital in determining the behavior, performance, longevity and cost effectiveness of the catalyst and the overall fuel cell. The authors made a complete review on support materials for PEMFC and DMFC electrocatalysts. The approaches that have been adopted to achieve better catalyst efficiency can broadly be divided into two categories: (i) employing Pt based bi-metallic and ternary catalyst systems and other non-precious metals to decrease Pt dependency and; (ii) improving the catalyst support. Conventionally, highly conductive carbon blacks of turbostratic structures with high surface are currently used as fuel cell electrocatalyst supports to ensure large electrochemical reaction surfaces. Over the last decade, researchers have been focused on nanostructured supports enabling faster electron and high electrocatalytic activity that are divided in two categories: carbon based/carbonaceous supports and non-carbonaceous supports [46]. Catalyst supports consisting of carbon nanomaterials with higher graphitic nature are reported to be more stable. Among non-carbonaceous based materials, titania, indium oxide, alumina, silica, tungsten oxide nanostructures, ceria, zicornia and conducting polymers have been widely investigated. The search for non-carbonaceous based supports is particularly essential to deal with the issue of carbon corrosion. The referred authors concluded that these novel electrocatalyst supports and improved catalyst loading techniques could bring revolutionary changes in the quest for high performance DMFCs. However, more detailed investigations (MEA studies, continuous cycling and accelerated degradation tests) are still required to understand the behavior of these materials under 'real' fuel cell conditions.

The diffusion layers do not participate directly in the electrochemical reactions but have the following important functions: allow the access of reactants to the catalyst active area; provide the removal of the products from the catalyst layer; electrically connect the catalyst layer to the flow field plate; allow heat removal and provide mechanical support to the MEA, preventing it from sagging into the flow field channels. These functions are best achieved by carbon fiber based materials such as carbon fiber papers and woven carbon fabrics or cloths. Carbon cloth is more porous and less tortuous than carbon paper, although carbon paper has excellent electronic conductivity. Diffusion media are generally made hydrophobic to avoid flooding in their bulk since the hydrophobic character allows the excess water in the cathode catalyst layer to be expelled from the cell. To fulfill these goals, typically, the gas diffusion layers are polytetrafluoroethylene (PTFE) treated. However, the anode diffusion layer of a DMFC should be hydrophilic to facilitate the mass transfer of the dilute methanol solution to the anode.

Different combinations of MEA's based on Nafion have been used. Most studies in the literature refer the use of Nafion 117 membranes based [18–21,23–32,35–37,41–43,47]. Hashim et al. [35] tested, in a passive stack, Nafion 117 with different catalyst loadings (2, 3 and 4 mg/cm^2) at the anode side using at the cathode side a 2.0 mg/cm^2 constant catalyst loading. The authors concluded that better fuel cell stack performances (12 mW/cm^2) were obtained for a catalyst loading of 3.0 mg/cm^2. In works [19–21] the MEA consists of two hot pressing wet-proof carbon papers which were used as the diffusion layer (anode: 4.0 mg/cm^2 Pt–Ru, cathode: 1.5 mg/cm^2 Pt), and a layer of Nafion 117 in between. Power obtained varies between 2.3 and 8.08 mW/cm^2. A GDL-24 BC was used in the work reported by Kamitani et al. [18] as the anode diffusion layer and for the air diffusion layer, a commercial gas diffusion layer LT-1400 was employed. For this active cell, the maximum power achieved was 12.5 mW/cm^2. Meng et al. [29] applied the anode with standard 4 mg/cm^2 total metal (TM) loading using 80% high performance (HP) Pt:Ru alloy (1:1 atomic ratio) on optimized carbon. The cathode was applied with 4 mg/cm^2 TM loading using unsupported HP Pt Black. The active cell tested achieved a maximum power of 12 mW/cm^2. D'Urso et al. [41] tested, in a planar fuel cell, a catalyst-coated membrane (CCM) containing separate anode and cathode layers on the same side. The CCM was coated with specific PtRu/C and Pt/C catalytic layers in correspondence to fuel and oxygen channels, respectively, to maximize the active area. A spray-coating technique was also employed to realize the catalyzed membrane. A Pt loading of 1 mg/cm^2 and 0.25 mg/cm^2 was used in the anodic and cathodic channel, respectively. The authors reported maximum power achieved of 1.3 mW/cm^2. Shen et al. [42] coated the Nafion 117 membrane with different catalysts. In the anode side Pt/Ru catalyst was used, supported on carbon black with metal content 60%, mixed with Nafion solution and isopropanol, giving a final Pt/Ru concentration of 5 mg/L and a catalyst/Nafion ratio of 7:3. In the cathode Pt/C (2 mg/cm^2) was deposited. The membrane was tested in a planar cell made of glass and the maximum output power was 0.5 mW/cm^2. A piece of catalyst coated membrane (CCM) composed by Nafion 117, an anode catalyst layer of Pt–Ru (4.0 mg/cm^2) and a cathode catalyst layer of Pt (2.0 mg/cm^2) was employed in references [24,30–32,43]. These membranes were tested in different kinds of cells. In air breathing cells [24,31] it was obtained

a maximum power output of 15.4 and 27.11 mW/cm^2. In active cells [30,32] the maximum power achieved was 115 mW/cm^2 and in a passive cell [43] was 7.4 mW/cm^2. A Nafion 117 membrane was also used in references [23,25–28,37,47] with an anodic catalytic load of 4.0 mg/cm^2 Pt–Ru and a cathodic catalytic load of 4.0 mg/cm^2 Pt. Regarding diffusion layers, carbon paper was used on both sides. These membranes were used in different cells. In active cells [26,37] was obtained a maximum power of 19.96 and 86 mW/cm^2. Regarding the membranes tested in air breathing fuel cells [23,25], a maximum power achieved was 14.79 and 34.2 mW/cm^2. Power outputs between 10 and 12 mW/cm^2 were obtained in passive fuel cells [27,28,47].

Lu et al. [22] used a Nafion 112 membrane pre-treated, the anode was ETEK with 5 mg/cm^2 Pt/Ru and the cathode was ETEK with 5 mg/cm^2 Pt. This membrane was tested in an active fuel cell and it was obtained a power output of 23 mW/cm^2.

In order to try to reduce methanol crossover, there are some works [40,48–51] that used innovative MEA's non-based on Nafion or with Nafion modifications.

Esquivel et al. [40] used a MEA based on a SU-8 polymer. The MEA fabrication consists in a series of steps that can be grouped in three main stages: (1) obtaining of the photoresist structures by the UV lithography process; (2) functionalization of the membranes by filling the cavities in the membranes with a proton exchange polymer and (3) carbon-based electrode deposition by air spray. The maximum power achieved with this membrane in a compact passive SU-8 fuel cell was 4.15 mW/cm^2.

A novel modification method of the commercial membrane Nafion 117 to produce an improved membrane for the MicroDMFC was presented by Liu et al. [48]. The method involves using γ-ray radiation and electroless palladium deposition on a Nafion 117 membrane. By reducing the membrane swelling ratio and methanol permeation, the single MicroDMFC with the modified Nafion 117 membrane produced reasonable power density performance as high as 4.9 mW/cm^2, almost doubled, only thanks to the modified Nafion 117 membrane. The main advantage of this modification method is easy to batch operation with low cost.

Kim et al. [49], used Pd nanophases in a Nafion polymer membrane electrolyte to enhance DMFC performance by preventing or reducing methanol crossover through the electrolyte. At high concentrations of methanol, such as 10 M, the power density of the Pd-impregnated Nafion membrane was higher than the one obtained with pure Nafion since methanol crossover was reduced. The authors conclude that Pd-impregnated Nafion membranes have the potential for use when operating with high concentrations of methanol.

Kanamura et al. [50] prepared successfully a new proton-conducting membrane consisting of uniformly macroporous silica and a proton-conducting gel polymer electrolyte. The prepared membrane exhibited high proton conductivity and low methanol permeation. The electrochemical performance obtained for the fuel cell with the composite membrane was similar to that obtained with the standard Nafion 117 membrane. From this result, it was concluded that the composite membrane consisting of ceramic and polymer can be applied to fuel cells working at low temperature.

Han et al. [51] prepared a new proton conducting membrane by confining sub-nanoliter volumes of perfluorosulfonic acid (PFSA) polymer within rigid pores cladded with zeolite layers. Tests showed that this membrane enables to obtain a maximum power output 900% higher compared to a standard MEA of Nafion 117 in a direct methanol fuel cell. The zeolites are believed to play an active role in the water and methanol managements through adsorption and transport, and the confinement of the PFSA within zeolite environment changes its microstructure resulting in the improved thermal stability.

Nafion 117 based membranes were used in almost all the works reviewed. Catalysts generally used are Pt–Ru at the anode side and Pt at the cathode side and loads vary from 1 to 4 mg/cm^2 at the anode side and from 0.25 to 4 mg/cm^2 at the cathode side. However, the most common values used are 4 mg/cm^2 for the anode side and 2 mg/cm^2 for the cathode side. Carbon paper is widely used as diffusion layer. Some new promising membranes developed in order to reduce methanol crossover were also presented.

2.3. Bipolar and planar design

Literature review discloses that the performance of a MicroDMFC depends not only on the types of fuel or oxidant, but also of an optimized design of flow plates and integration of a proton exchange membrane (PEM). Bipolar and planar designs are the two basic designs used in MicroDMFC for the oxidant and fuel delivery. Traditional bipolar MicroDMFCs exhibit the capability to deliver higher electrical power densities, however, complex microfabrication processes and rather cumbersome membrane assembly technology present obstacles towards industrialization [6]. A monolithic fuel cell, in which the anodic and cathodic microchannels are formed in one planar substrate, as first proposed by Motokawa et al. [52], allows easy prototyping and reduces the complexity of the membrane assembly process. In planar design, the fuel and oxidant channels are interdigitated and both electrodes are on the same side. This design is more suitable for a monolithic integration but requires a larger surface area to deliver similar performance [16]. Both designs are represented in Fig. 1.

Planar design was used by studies [36,41,42]. Power outputs achieved with these cells vary between 0.5 and 3 mW/cm^2. Tominaka et al. [53] proposed a novel design for a microfuel cell consisting in on-chip power source with the demonstration of its fabrication and operation to prove the concept. The design of the on-chip cell concurrently realizes air-breathing, membraneless, and monolithic structures. Its simple design is important from the viewpoints of fabrication (e.g., replication), integration, and compatibility with other microdevices. The prototype cell proved that the concept, to generate electric power without pumps, was valid. Although the net performance was higher than that of other on-chip fuel cells, the authors believed that optimizing the loading of catalysts and/or the microstructures of electrodes (for example, by adding an ionomer to the cathode in a technique similar to that for

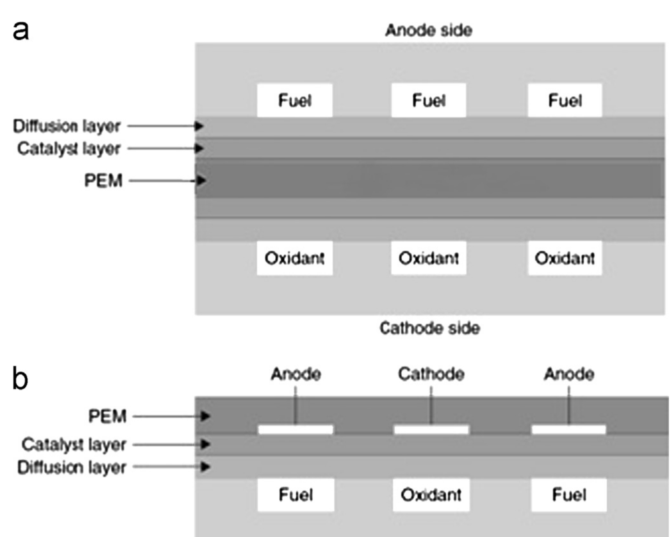


Fig. 1. Two basic fuel cell designs: (a) Bipolar and (b) Planar, adapted from Nguyen et al. [14].

conventional fuel cells) would result in further performance improvement.

Planar fuel cells are very attractive because of easy prototyping and reduced complexity of the membrane assembly process. There are some works using this design, however fuel cell performances reported with this kind of cells are lower than the ones reported for conventional bipolar fuel cells. A novel design of an on-chip cell was proposed in a recent work. Further improvements are needed to enhance the performance of planar cells.

2.4. Fuel and oxidant delivery system

The fuel and oxidant can be supplied to a MicroDMFC in an active or a passive way as already explained. Active systems use external components such as a pump or blower, a fan for cooling, reactant and product control, allowing the operation at favorable conditions with respect to temperature, pressure, concentration and flow rate. Evidently, this improves flow mass transport and electrochemical activity, therefore higher current density and power can be achieved. This type of system supply has greater costs and lower system energy density, so, it is better suited for large fuel cells. Passive systems do not need external accessories; they use natural capillary forces, diffusion, convection (air breathing) and evaporation to achieve all processes without any additional power consumption. They usually operate at low current densities resulting in reduced cooling loads, less water management issue, less heat production and lower required fuel delivery rate. Therefore, by using a well designed compact architecture, a passive system is more suitable for portable power sources. However, these feed systems cause lower system performance due to the difficulty in getting a continuous and homogeneous supply of reactants to the anode and cathode. The lack of flowing force to remove the bubbles that constantly build up from the formation of carbon dioxide, in the anode reaction, also hinder further oxidation of fuel at the anode surface. At the cathode, water droplets tend to build up and block the active surface, thus reducing the oxygen supply. System control associated with water and methanol management adds considerable complexity to passive DMFC systems, particularly those being developed for portable applications.

Most of the researchers are presently interested in overcoming these difficulties and achieving optimized low cost passive fuel cells with a growing number of references dealing with passive designs [27,28,34,35,40,43,47,50]. In references [27,28] a passive hybrid silicon based micro-direct methanol fuel cell was proposed as a power solution in the MEMS field. From the results obtained it can be concluded that the fabricated device can be considered as a working demonstrator and a good starting point for the development of micro-fuel cells based on microfabrication technology. Hashim et al. [35] designed, fabricated and tested a passive single-cell and a multi-cell stack with a novel cathode plate structure and assembly layer. The maximum power obtained for the stack was 12 mW. Esquivel et al. [40] presented a based SU-8 passive fuel cell. The system was based on a diffusion-driven feeding of methanol and air, with reduced complexity allowing elimination of all auxiliary devices. The current collectors were provided with a grid of through-holes that allow delivering the reactants to the MEA by diffusion. For this cell, the maximum power achieved was 4.15 mW/cm^2. Sun et al. [43] tested a self-pumping MicroDMFC with polymer bipolar plates, enabling the circulation of methanol solution using the energy from the expansion of carbon dioxide. The mechanism of self-pumping was explained by a simple two phase fluid model. The fuel cell works along different orientations, even making the bubble moving when the channel is placed upside down. The self-pumping fuel cell could reduce the volume, simplify the electrical connections and omit an extra pump to force the circulation of the fuel. The maximum power obtained was 7.4 mW/cm^2. Esquivel et al. [47] evaluated the influence of current collector open ratio on the performance of a passive MicroDMFC. The device was based on a hybrid approach, consisting of two micro fabricated silicon current collectors assembled together with a commercial membrane electrode assembly. Results showed that the way in which the open ratio of current collectors was combined had an effect not only on the output power but also on the repeatability of polarization curves. The results obtained indicate that a dissimilar open ratio of current collectors can yield better performance than a symmetric arrangement. This cell achieved a maximum output power of 12 mW/cm^2.

Due to cost reduction and design simplicity, passive methanol fuel cells, due to their enormous potential for portable applications, are attracting much attention and will certainly be further developed in the next years. There are some interesting studies with passive fuel cells available in literature. There are also some studies with air-breathing cells (a device to fuel supply is needed). However, fuel cells power densities obtained with this kind of cells are lower than the ones reported for active fuel cells.

2.5. Flow field effect

Once the reactants enter the cell, they must be distributed over the entire active area. This is typically accomplished through a flow field, which may be in a form of channels covering the entire area in some pattern or porous structures. The main task of these is to guarantee distribution of fuel and oxidant over the reaction surface area as well as the removal of products from the cell. Different types of flow pattern designs for active DMFCs are presented in the literature. The most commonly used flow fields are (a) parallel, (b) spot (or grid), (c) serpentine and (d) interdigitated channels, as shown in Fig. 2.

The flow field most widely employed in MicroDMFC is based on the serpentine configuration [24]. In such a configuration, the reactant is constrained to flow in a zigzag way along parallel channel. In general, different flow field designs have advantages

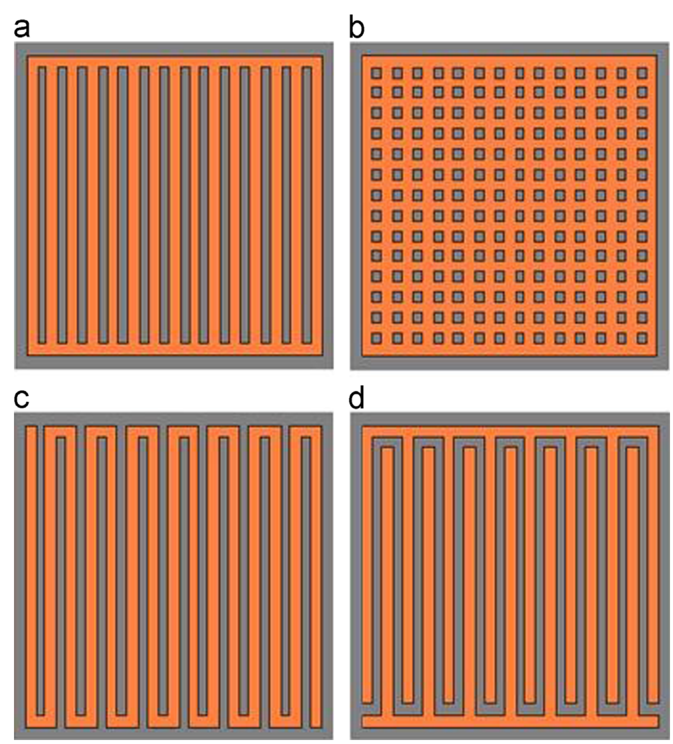


Fig. 2. Representation of the most commonly used DMFC flow fields: (a) parallel, (b) spot (or grid), (c) serpentine and (d) interdigitated channels.

and disadvantages associated with their application. Proper selection of flow fields with respect to the MicroDMFCs operational and application conditions can help to achieve cost and performance goals.

Ghayor et al. [34] evaluated fuel cell performance using cross strip and parallel flow fields. Performance was better using cross strip flow field because this configuration increased the methanol contact surface with the MEA. Two flow field designs (parallel and serpentine) were studied by Weinmueller et al. [37] at the anode while the cathode flow channels follow the serpentine design (active area of 1 cm^2). In direct comparison of the two different flow fields at the anode, the serpentine flow field showed an average increased open current potential of $+10$ mV, higher power densities of up to 22 mW/cm^2 and larger current densities of up to 150 mA/cm^2 than for the parallel flow field. Lu et al. [22] evaluated the performance of an active fuel cell (active area of 2.25 cm^2) using four different types of flow fields: mixed multichannel serpentine with wide channels, single serpentine, double serpentine and mixed multichannel serpentine with narrow channels. Under the conditions described in the study, MicroDMFC with double-channel serpentine flow field had the best performance and MicroDMFC with the mixed narrow multichannel serpentine flow field presented the worst performance. Wang et al. [23] evaluated (experimentally and by 3D simulations) the effect on an air breathing cell performance of four different types of flow field: double serpentine, parallel, helix and single serpentine (active area of 1.44 cm^2). Simulated results indicated that the double serpentine flow field showed better flow velocity distribution and more uniform temperature distribution, which might lead to a better performance of the MicroDMFC. Further experimental investigation on the four types of flow fields also confirmed that the MicroDMFC with double-serpentine flow field structure exhibits a maximal power density at a variety of inlet velocities, which is in good agreement with the simulated results. A flow field design N-Inputs-N-Outputs parallel with rectangular convexes (active area of 0.64 cm^2) to reinforce methanol mass transport and reduce concentration polarization was presented by Zhang et al. [26]. Experimental and simulation studies were done and both indicated that fuel cell performance can be enhanced by the use of this flow field scheme. Zhang et al. [24] also reported a study with a new flow field design (tapered single serpentine with an active area of 0.64 cm^2). Compared with conventional single serpentine design, the new flow field is able to enhance the pressure difference between any of the adjacent flow channels and thus improve the mass transport efficiency and the exhaust resultant rate utilizing the simulation analysis. Different cell configurations (different distances between anodic and cathodic channels) in a planar fuel cell were studied by D'Urso et al. [41]. A maximum power density was achieved at room temperature with the smallest distance between anode and cathode (0.25 mm). Similar performance was obtained with the largest distance between anode and cathode (0.5 mm) by using 10 M methanol concentration at the anode.

Serpentine configuration (single or double) was used in the most part of the works reviewed. Fuel cell performance is enhanced with this kind of channels configuration. An example of a new serpentine configuration was presented – tapered serpentine – leading to better fuel cell performances than the ones reported for serpentine. This new configuration seems to be an excellent alternative to conventional serpentine, although, more work on this issue is needed.

3. Operating conditions

3.1. Methanol concentration effect

The effect of the methanol concentration on the DMFC performance generally reflects two phenomena: increases on the methanol concentration lead to an increase on the coverage of the electrocatalyst sites by methanolic species, but also increase the concentration gradient between the anode and cathode side with a consequent increase in the crossover through the Nafion membrane. This requires a delicate balance among the effects of methanol oxidation kinetics and methanol crossover in order to enhance the performance of a DMFC. Another point that should be accounted for is the fact that the polarization behavior in the mass transfer region is directly related to the methanol concentration, so an increase in the limiting current density is achieved with an increase in methanol concentration.

There are some studies in literature evaluating the methanol concentration effects. According to the data presented by Zhang et al. [19] the cell performance of a cell with an active area of 0.47 cm^2 increased with methanol concentration from 0.1 to 2 M methanol solution. For the high concentration tested (4 M) the performance decreased rapidly. This phenomenon is due to the high methanol crossover. In another study [30] the influence of methanol concentration was studied for 0.5, 1.0, 1.5, 2.0 and 2.5 M. Best fuel cell (active area of 0.64 cm^2) performance was found for a methanol concentration of 1.5 M. When higher methanol concentration was used, excess methanol remains after the electrochemical reaction, inducing methanol crossover and generating overpotential at cathode, which degrades the cell performance. On the contrary, lower methanol concentrations could not provide sufficient reactants to join the reaction, especially at high current densities. It was also noted that the optimal methanol concentration of 1.5 M validated in this work is higher than the concentration of around 1 M, more suitable for DMFCs with larger sizes [54,55]. This is mainly due to the fact that the methanol transport in micro-sized DMFCs is more difficult, so a higher methanol concentration is required. The effect of methanol solution was also evaluated for 1, 2, 3, 4 and 5 M in a fuel cell with 2.25 cm^2 of active area by Lu et al. [22]. Results also showed that higher concentration of methanol solution brought better performance for MicroDMFCs. When the concentration of methanol solution is 1 M, three stages, kinetic polarization, ohmic polarization and mass transport limitation, could be observed on the polarization curves. When higher concentrations of methanol solution were used, the mass transport limitation disappeared in the polarization curves. The effect of methanol concentration was also studied by Zhang et al. [32] on a 0.64 cm^2 fuel cell. Methanol concentrations varying from 0.5 to 2.5 M were supplied to the cell in order to study their effect on dynamic response. The authors concluded that output voltage stability of the cell at 2.5 M was better than that at 0.5 M, 1.5 M and 2.0 M. But output voltage at 2.5 M was lower than that at 1.5 M and 2.0 M. With respect to response time, stability and output voltage, dynamic responses at 1.5 M and 2.0 M were a better compromise compared with those at other methanol concentrations.

The authors from [31,33] evaluated cell performance (on an air breathing cell with 0.64 cm^2 of active area) feeding methanol solutions of five different concentrations (0.25, 0.5, 1, 1.5 and 2 M) and concluded that the open circuit voltage was higher for lower methanol concentrations and that the best performance was obtained for a methanol concentration of 1 M.

Esquivel et al. [28] tested a passive micro-fuel cell with an active area of 0.28 cm^2 at methanol concentrations of 0.1, 1, 2, 3 and 5 M. It was concluded that fuel cell power increased with methanol concentration, reaching a maximum value at 5 M. This power density was higher than any of the values reported before in silicon-based methanol fuel cells without external fuel pumping [6] and close to the values reported for stainless-steel fabricated passive micro cells [56,57]. Hashim et al. [35] studied the effect of methanol concentration in a passive fuel cell of 1 cm^2 active area increasing methanol concentration from 1 to 5 M. The authors

concluded that fuel cell performance increases by increasing methanol concentration up to 4 M but decreases dramatically when increasing to 5 M because of methanol crossover. The effect of methanol concentration was also studied by Sun et al. [43] in a passive fuel cell with an active area of 5 cm^2 for 1, 2, 3 and 4 M. It was verified that cell performance increased when methanol concentration increased from 1 M to 3 M. This is because more methanol molecules can be catalyzed on the surface of catalyst when using higher concentrated methanol. However, the peak power density decreased when the fuel concentration is 4 M. The reason is that the effect of the potential generated from methanol crossover exceeds the one of the concentration of methanol molecules close to the anode catalyst.

The works reviewed on MicroDMFC reported different optimal methanol concentration. There is no consensus regarding this issue but the trend is that the optimal methanol concentration is higher than the value usually found for DMFC. The effect of methanol concentration seem to overlap the effect of operating conditions (flow rates mainly), reactants delivery system and even fuel cell area.

3.2. Flow rate effect

Efficient removal of carbon dioxide gas bubbles and liquid water produced at the anode and cathode side, respectively, must be maintained to allow reactants to reach catalyst sites. Removal of carbon dioxide slugs and prevention of cathode “flooding” can be achieved by increasing flow rates (in active fuel cells). However, increasing flow rates requires more pumping power. A very high flow rate at the cathode will dry out the polymer membrane, decreasing proton conductivity and hence cell performance.

There are some studies available in literature studying the effect of flow rates on micro-fuel cell performance.

Kamitani et al. [18] characterized the room temperature performances of miniaturized MicroDMFCs having small active areas (<0.4 cm^2) at low forced input fuel flow rates (<10 uL/min). The study showed that improved cell performances in terms of power density can be achieved at low flow rates by (i) reducing the fuel cell area and (ii) reducing the micro-channel cross section. The study also revealed that higher fuel use efficiencies can be obtained at a lower flow rate. To investigate the effect of the anode flow rate, a micro-methanol fuel cell was tested by Zhang et al. [30] using 1.5 M methanol solution at five different flow rates (0.25, 0.5, 1.0, 2.5 and 5.0 ml/min) at 40°C. The effect of the anode flow rate on cell performance was somewhat difficult to explain. Although the overall highest power density was achieved at 1.0 ml/min, the optimal anode flow rate for best performance was not consistent at different current densities. Based on the testing results, a novel “shifting-rate” feeding method was introduced in this work to optimize the anode feeding mechanism and was shown to be feasible. Liu et al. [33] also analyzed the influence of anode flow rate for a fuel cell stack. Five different anode flowrates (1.0, 2.0, 3.0, 4.0 and 5.0 ml/min) were used in a cell with an active area of 0.64 cm^2. The author concluded that the stack performance increased with the flow rate. Weinmueller et al. [37] studied the influence of anode flow rate for 0.035, 0.14 and 0.56 ml/min using parallel and serpentine channels at the anode. With a parallel flow field at the anode and a serpentine flow field at the cathode the variation of the volumetric flow rate had yielded an optimal at 0.14 ml/min of a 1 M methanol solution. For a serpentine flow field at the anode side (and also serpentine flow field at the cathode side) an increase in volumetric flow rate (anode side at a constant O_2 gas flow rate of 8 ml/min) at the cathode side achieved a higher electrical performance. The optimal anode flow rate depends therefore of the channels flow design. The authors from references [31,33] evaluated the cell performance (active area of 0.64 cm^2) for seven different anode flow rates and concluded that the OCV continuingly decreased with the increment of the flow rates. It was justified that the increment of the anode flow rate could accelerate the methanol crossover rate. The testing results showed that the optimal anode flow rate of the cell was 1.0 ml/min. In addition, from 0.4 to 1.2 ml/min, the variation of the cell maximum power density was not significant. The influence of cathode flowrate was not evaluated because the cell studied was self breathing. Lu et al. [22] also studied the effect of methanol flowrates in MicroDMFCs (active area of 2.25 cm^2) with four kinds of flow fields. For the multi-channel serpentine with mixing, the performance became better with high flowrates. In the single and double-channel flowfields, the performances were enhanced increasing methanol solution flowrate from 0.0503 to 0.1128 ml/min. However, the performance of these two MicroDMFCs became worse when the flow rates of methanol were further increased from 0.1128 to 0.3479 ml/min. Wang et al. [23] evaluated the effect of inlet anode flow velocities of 0.01, 0.005 and 0.001 m/s and concluded that cell performance (active area of 1.44 cm^2) was enhanced by the increase of inlet flow velocity. To study the effect of methanol flow rate to the cell (active area of 0.64 cm^2) on dynamic condition, Zhang et al. [32] varied the supply flow rates of methanol solution from 0.25 ml/min to 5.0 ml/min. All dynamic responses at different methanol flow rates showed excellent stability, repeatability and rapidness. Response speed increased with increasing methanol flow rate while output voltage decreased. Increasing anode flow rate is beneficial to improve removal of CO_2 bubbles, resulting in the increase of response speed. The reduced amount of CO_2 gas decreases transport resistance of methanol, and the increased flow rate raises convection velocity of methanol solution: these two factors enhance methanol transportation rate resulting in more serious methanol permeation.

Different optimal methanol flowrates were proposed for active MicroDMFC by the available literature. Some authors report different methanol flowrates depending on channels design and also on current densities. Obviously, depending of fuel cell area, different ranges of methanol flow rates are required. Generally, fuel cell performance increases with methanol flow rate increase but just to a certain optimal value.

3.3. Heat management

Controlling the operating temperature and the heat transfer management are critical to obtain optimized MicroDMFC performances. It is commonly believed that an increase in the operating temperature in a certain range can lead to a marked increment in cell performance [20]. The expected benefits of increasing the temperature are the following: increased activity of the catalysts, reduction in the membrane resistance and increased mass transport in the cell. However, for portable applications it is desirable to operate to room temperatures to avoid auxiliary devices. For this reason most of the researchers work at room temperature and try to obtain an optimized heat management [14]. Active control of temperature will however be necessary if the micro-fuel cells are operating at extreme climates or unconditioned temperatures. At the cathode side, the methanol that crosses the membrane react producing heat. According to Kamarudin et al. [6] methanol crossover increased with the increased methanol concentration, thus increasing the cell temperature which leads to enhanced reaction kinetics at both the anode and cathode. The heat produced has to be dissipated, or else the accumulated heat in the system might be a strong disadvantage for compact portable systems.

Zhang et al. [20] studied the influence of cell temperatures resulted from current applied to a heater included on fuel cell

design. When the currents applied to the heater are 53.9, 41.5, and 0 mA, respectively, the corresponding operating temperatures measured by the sensor are 58, 42 °C and room temperature (25 °C). The experimental results showed that the fuel cell performance duplicates when the operating temperature increases from 25 °C to 58 °C. Zhang et al. [30] found, in the course of their experiments, that the variation in cell performance with changes in the operating temperature was not uniform. The experiments were conducted at 40, 60 and 80 °C. Contrary to the expectations, the best cell performance was not obtained at the higher operating temperature. Although the cell performance was better at 80 °C when the current density is less than 260 mA/cm^2, once the current density exceeded this value, operation at 60 °C showed better performance. It appears that this unexpected temperature dependence was a consequence of the anode flow rate (1.0 ml/min) being insufficient to provide either an adequate methanol transport rate for the rapid oxidation reaction or an efficient removal rate of the large amounts of CO_2 bubbles generated at high current densities. To test this hypothesis, the authors increased the anode flow rate to 2.5 and 5.0 ml/min while keeping the other operating conditions constant. At a higher flow rate, the cell performance at 80 °C was effectively much better than at 40 or 60 °C. The authors concluded that in order to ensure the best cell performance at different operating temperatures, the anode flow rate must be regulated. This finding is important bearing in mind future applications. Weinmueller et al. [37] founded that the effect of rising temperature for serpentine and parallel flowfields resulted in a generally improved power density at operating conditions used in the work. Ghayor et al. [34] studied the influence of temperature for an active and a passive fuel cell for 30, 40, 50 and 60 °C and concluded that for both types of cells, the performance increases for increasing temperature. 3-D simulations were used in the work reported by Hsieh et al. [58] to investigate the heat transfer in a micro-direct methanol fuel cell with serpentine flow fields. The authors concluded that a relatively uniform temperature can be obtained for straight channel portions. As the flow approaches the bend region the temperature field in these regions is significantly distorted accompanying the corresponding velocity vector profile.

Generally, fuel cell performance is improved with increasing temperatures. Some authors concluded that the impact of temperature on performance increases with increasing flow rates. However, for portable application it is advantageous to work at room temperature, so high temperatures should be avoided. The main research target is operation at ambient temperature with an optimized uniform temperature distribution through the cell.

3.4. Innovations

The main goal of researchers is to improve fuel cell performance. Innovations, in different fields, have been proposed to fulfill this objective [19–21,25,29,31,40,59,60].

Meng et al. [29] integrated an embedded self-circulation structure into a MicroDMFC to actively deliver liquid fuel to the anode microchannel and agitate the fuel without any discrete power consuming pumping component. The structure also achieved orientation-independent gas removal, without introducing an additional gas separator. Simultaneous elimination of the two auxiliary components (i.e., the gas separator and the liquid pump) reduced the energy and power density of the system. The fuel circulation was verified by continuous operation of the system for over 70 min, as well as visual confirmation. The proposed mechanism provides an anode-side example for passive balance of plant components for the next-generation MicroDMFCs. Zhang et al. [19] presented a novel anode structure with microblocks, which stir the methanol solution and make the liquid undulate through the whole channel. Modeling and experimental data were presented and showed that this novel design more than duplicates fuel cell performance. Another design innovation, a silicon-based air-breathing micro-fuel cell stack with a shared anode plate and two-air breathing cathode plates, was presented by Wang et al. [21]. Three MicroDMFC stacks with different types of anodes were assembled, and characterized together with a single cell. Simulation and experimental results showed that the MicroDMFC stack with fuel transport in a shared model had the best performance, achieving a power density almost twice the one obtained in a single cell.

A high efficient passive water/air management device was proposed by Peng et al. [59]. The apparatus consisted of a cornered micro-channels and air-breathing windows with hydrophobicity arrangement to regulate liquids and gases to flow on their predetermined pathways. The device was fabricated by SU-8 molding and selective surface modification processes. The system yielded a water removal rate about 20 times faster than the water generation. Droplets were quickly removed wherever they emerged due to strong wettability gradient at the hydrophobic/hydrophilic interface exactly located at an acute junction. The fuel cell operating with this device exhibited improved durability and more stable current output. Zhang et al. [31] presented a perforated structure with parallel flow channels as cathode current collectors. Compared with the conventional cathode perforated structure, the simulation results indicated that the improved one could enhance the oxygen mass transport and reduce the water flooding to improve the cell performance. This work also used a stainless steel mesh in order to improve fuel cell performance, similar to works [30,32]. The stainless steel mesh was able to mitigate methanol permeation and to accelerate removal of CO_2 bubbles due to its mesh structure, improving output voltage and response speed of the cell.

The innovation reported by Zhang et al. [25] consisted of a silicon-based self-breathing MicroDMFC with a new spoke cathode structure using MEMS technology. To prove the superiority of the new cathode structure, a three-dimensional model was implemented. Compared to the conventional perforated cathode structure, the new one could improve the cell performance and water removal due to an increase in oxygen transport efficiency and pressure on the catalyst layer. Moreover, the stability tests of the self-breathing MicroDMFC demonstrated that the spoke structure could remove the water in the cathode effectively. From the results obtained in this work, was concluded that the self-breathing MicroDMFC with the new cathode structure could have potential advantages in the development of high power sources for portable electronic devices and MEMS.

Esquivel et al. [40] presented a novel approach to an all-polymer micro-fuel cell based on SU-8 photoresist. All fuel cell components (current collectors and MEA) were fabricated with the same material, whose bonding capabilities were exploited to obtain a highly compact device. The integration was achieved in two steps: embedding of a polymeric electrolyte into a porous SU-8 membrane and bonding all SU-8 components together. The micro-fuel cell has been first characterized using an external casing or frame to validate the functionality of its components. Despite the simplicity associated to the passive delivery of the fuel and the low catalyst content, the performance of the micro-fuel cell was comparable to the few polymeric devices reported to date. After validation, all components were bonded together by hot-pressing in order to obtain the compact device. Characterization of the assembly showed a decrease in power density due to an increase in contact resistance. However, the drastic reduction of the device dimensions when dispensing with the external frame resulted in a larger volumetric power density. The authors suggest further work directed to device optimization through the

reduction of ohmic losses. Nevertheless, the results presented demonstrate the potential of this approach to obtain a fully polymeric power source. Moreover, the use of this technology offers additional opportunities for integration of micro-fuel cell within a wide variety of polymeric devices such as lab-on-chip and other microfluidic platforms.

A single cell micro-direct methanol fuel cell, used in works [37,60] was investigated using electrochemical impedance spectroscopy. AC impedance spectroscopy was used to separate contributions to the overall cell polarization from the anode, cathode and membrane. A clear distinction between the different electrochemical phenomena occurring in the MicroDMFC, especially the distinction between double layer charging and Faradaic reactions was shown. Analysis of impedance data revealed that the performance of the tested cell was largely limited by the presence of intermediate carbon monoxide in the anode reaction. Higher temperatures increased cell performance by enabling intermediate CO to be oxidized at much higher rates. The results also revealed that serpentine anode flow microchannels showed a lower tendency to intermediate CO coverage and a more stable cell behavior than parallel microchannels.

Zhang et al. [20] integrated a heater and a temperature sensor in a MicroDMFC. The authors showed that it was possible to enhance the cell performance by adjusting the heater and imposing an optimal temperature enabling the cell operation under extreme environments

New cell designs and innovations on fuel deliver system were presented with the main purpose of solving the problems related with water management and methanol crossover, the most complicated issues regarding MicroDMFC technology. Some important innovations were suggested, namely a high efficient passive water/air management device. Work on hydrodynamic characterization of two-phase flows is still missing in the micro-fuel cell channels (in the anode and cathode sides).

3.5. Performance comparison

Table 2 summarizes the basic parameters reported in the works analyzed in the present review.

Analyzing the table some general conclusions can be drawed. The membrane used in almost all the works reported is Nafion 117. The temperature used in the fuel cells reported in the works reviewed is predominantly room temperature, the operation condition of interest in portable applications. Regarding the fuel and oxidant supply, three different types were found in literature reviewed: active, air-breathing and passive. As expected, better power densities are generally obtained for active fuel cells, but passive fuel cells while having lower performances are more

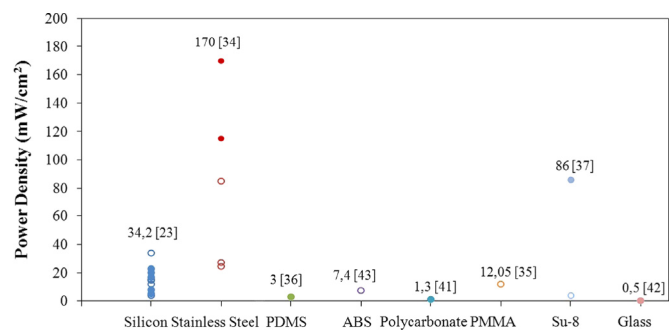


Fig. 3. Maximum power density of the different carrier substrates used – filled dots correspond to active fuel cells and open dots correspond to air breathing and passive fuel cells.

Table 2
Basic parameters reported in the works analyzed in the present review.

Ref.	1st author	Year	Type	Active area (cm^2)	Substrate	Design	PEM	P_{max} (mW/cm^2)	C_{CH_3OH} (M), Q_{CH_3OH}/Q_{Air} (ml/ min)	T (°C)
[27]	Torres	2008	Passive	0.28	Silicon		Nafion 117	10	4 M	25
[18]	Kamitani	2008	Active	0.3	Silicon	Serpentine	Nafion 117	12.5	3 M, 0.005/30	25
[28]	Esquivel	2008	Passive	0.28	Silicon		Nafion 117	11,4	5 M	25
[29]	Meng	2009	Active	2.5	Silicon	n.r.	Nafion 117	17	2 M, 3/100 O_2	20
[36]	Shen	2009	Active		PDMS	Planar	Nafion 117	3.0	1 M, 0.05/0.16	20
[19]	Zhang	2009	Active	0.47	Silicon	Serpentine	Nafion 117	8.08	2 M, 0.6/40 O_2	20
[47]	Esquivel	2009	Passive	0.28	Silicon		Nafion 117	12	2 M	20
[20]	Zhang	2009	Active	0.47	Silicon	Serpentine	Nafion 117	5.55	2 M, 0.1/n.r.	56
[35]	Hashim	2009	Passive (6 cell stack)	1.0	PMMA		Nafion 117	12.05	4 M	20
[21]	Wang	2009	Air-breathing	0.6	Silicon	Serpentine	Nafion 117	2.3	2 M, 0,40	25
[34]	Ghayor	2010	Active	n.r.	Stainless steel	Cross strip	n.r.	170	2 M, 0.4/n.r.	60
[34]	Ghayor	2010	Passive	n.r.	Stainless steel		n.r.	85	2 M	60
[30] [32]	Zhang	2010	Active	0.64	Stainless steel	Parallel	Nafion 117	115	1 M, 1/50 O_2	80
[37]	Weinmueller	2010	Active	1	SU-8	Serpentine	Nafion 117	86	1 M, 0.14/8	88
[40]	Esquivel	2010	Passive	0.25	SU-8		Nafion filled SU-8	4.15	4 M	40
[33]	Liu	2010	Air breathing Stack	0.64	Stainless steel	Parallel	n.r.	24.75	1 M, 5.0	20
[31]	Zhang	2011	Air breathing	0.64	Stainless steel	Parallel	Nafion 117	27.11	1 M, 1	20
[22]	Lu	2011	Active	2.25	Silicon	Double serpentine	Nafion 112	23	5 M, 0.0503 /50	20
[23]	Wang	2011	Air breathing	1.44	Silicon	Double serpentine	Nafion 117	34.2	2 M, n.r.	25
[24]	Zhang	2011	Air breathing	0.64	Silicon	Tapered serpentine	Nafion 117	15.4	1 M, 1	20
[25]	Zhang	2011	Air breathing	0.64	Silicon	Serpentine	Nafion 117	14.79	1 M, 1	20
[26]	Zhang	2011	Active	0.64	Silicon	Rectangular-convex NINO	Nafion 117	19.96	1.5 M, 0.5/50 O_2	20
[42]	Shen	2011	Active	0.11	Glass	Planar	Nafion 117	0.5	1 M, 0.06/0.16 H_2O_2	20
[41]	D'Urso	2011	Active	n.r.	Polycarbonate	Planar	Nafion 117	1.3	2 M, 1/40 O_2	20
[43]	Sun	2011	Passive	5	ABS	Parallel tapered	Nafion 117	7.4	3 M	20
[51]	Han	2012	Passive	n.r.	Stainless steel		Nafion PFSA	30	2 M	60

n.r. – Not reported.

interesting bearing in mind the target market of portable applications. Relatively to channels design and cell type, some cells are planar and, in conventional design, serpentine channel design is the most common. The substrates more used are silicon and stainless steel with a relatively wide range of power densities achieved as sketched in Fig. 3 for both active (filled dots) and passive (open dots) cells.

Better performances were achieved for active fuel cells corresponding to carrier substrate in stainless steel. Comparing passive and air breathing fuel cells made on silicon or stainless steel, the performance difference is not so pronounced. Some alternative polymers were tested but the performances are still very poor, except for the active fuel cell using SU-8 [37]. From the polymers used in the literature reviewed, SU-8 seems to be the most promising one [37].

3.6. Cost analysis

Despite of the advances on new materials and manufacturing techniques presented in the previous sections, the MicroDMFC's did not enter in the market as an alternative to the batteries technology. In the literature, there are some works referring DMFC or MicroDMFC global costs. One of the earliest works, by Hockaday et al. [61], presented a market analysis comparing a MicroDMFC with a new design allowing vacuum deposition techniques to be used in the mass production, with a lithium battery. The authors referred that an acceptable cost for small power devices (<1 W) was around \$100/W. Given this analysis, the cost of the MicroDMFC presented is clearly below this level. Based on a detailed review of patents and technical papers, Apanel et al. [62] designed a DMFC engineering concept for three mobile applications: cell phones, small portable generators, and automobiles. They concluded that DMFCs for cell phones and small portable generators are below the cost of conventional power technologies. Kamarudi et al. [63] included in their work a section of cost and commercialization for DMFC where some works with the final goal of diminish the fuel cell cost were referred. The authors concluded that DMFC technology cost is competitive due to the large market size and economies of scale. However, methanol crossover is currently the biggest challenge faced by DMFC designers as it has the most effect on the cell performance. The same authors published an overview on the challenges and developments of MicroDMFC [6] and also concluded that the MicroDMFC systems are eventually far less expensive than the alternative battery technologies in the long run. Rashidi et al. [64] compared a Li-ion battery with a DMFC to supply the power for a laptop, camcorder and a cell phone. A parametric study of the systems for an operational period of 4 years was performed. Taking into account the assumptions made for the Li-ion battery and DMFC system, the authors concluded that battery cost is lower than the DMFC during the first year of operation. However, by the end of 4 years of operational time, the DMFC system would cost less.

The works published referring issues related with DMFC massive commercialization are very optimistic and predicted that soon this technology will replace conventional power sources, specially for portable applications. However, all the works cited were published at least 4 years ago and the optimistic expectative is not yet entirely achieved.

3.7. Modeling studies

Fuel cell modeling has received much attention over the last decade in an attempt to better understand the phenomena occurring within the cell. The necessity of formulation of adequate mathematical models is based on the need to reach a deeper understanding of internal processes (reactions, mass transport and heat transport). Most of these processes are difficult to follow directly in experiments and mathematical model can be applied to obtain hints for the development of optimal control and operating strategies. Different types of approaches are usually followed. Analytical models, for example, are an adequate tool to understand the effect of basic variables on fuel cell performance. Many simplifying assumptions are made to develop an approximate analytical voltage versus current density correlation. Semi-empirical models predict the fuel cell performance as a function of different operating conditions (such as pressure, temperature or fuel concentration) using simple empirical equations. Mechanistic models are transport models using differential and algebraic equations whose derivation is based in the electrochemistry and physics governing the phenomena taking place in the cell. These equations are numerically solved by different methods. In literature some mechanist models, with different degrees of complexity, are presented for MicroDMFC.

Kamitani et al. [18] used a multi-parameter 2D model, already developed for DMFC. This model uses the Fick's Law and Tafel equation. Analytical solutions enabled the calculation of concentrations of methanol and oxygen present at the anode and cathode microchannels and at the anode and cathode catalytic layers; from these data the fuel cell electrical performances could be predicted for a given set of parameters. The model did not take into account carbon dioxide generation and ignored the pressure gradient along the anode microchannel, so it fails to predict the enhanced performances observed when the microchannel height is reduced. Zhang et al. [30] developed a 2D mathematical model. The model was based in some simplifications, i.e. steady-state conditions were assumed, only single phase was considered in GDL and the CL was considered as interface. Although the simulation and testing results were qualitatively similar, the magnitude of the simulation results was generally about two-thirds of the experimental results. This occurred probably due to the simplifications assumed and to the inadequate choice of model parameters. A 2D steady-state model was developed by Liu et al. [33] assuming several simplifications: (1) the single cell is isothermal; (2) two-phase flow due to the CO_2 gas or liquid water is neglected; and (3) the catalyst layer is simplified as an interface between the diffusion layer and the proton exchange membrane. Approaches of mass transport in diffusion layers and anode flow field are mainly composed of diffusion and convection, respectively. The model was used to predict values of maximum cell power at different methanol concentrations and good agreement with experimental results was obtained.

Three dimensional simulations obtained with CFD code Fluent were described by Hsieh et al. [58] to investigate the flow and heat transfer for developing laminar flow in the micro-direct methanol fuel cell with serpentine flow fields. This study demonstrated that CFD could be employed in micro-fluidics with liquid as working medium in the channel at $Re < 421$. The same type of modeling approach was used by Zhang et al. [19] to optimize the MicroDMFC performance. It was assumed that the cathode over-potential was constant on condition that sufficient pure oxygen gas was supplied. In order to reduce the computational complexity several assumptions were made: steady-state, isothermal operation, laminar flow in channels, isotropic porosity in MEA and single-phase flow when the CO_2 production was neglected. The flow field design used in the simulations consisted in several channels with microblocks varying in number and dimensions. This implemented 3D model was further applied in a work of the same authors [21] to analyze the performance of a MicroDMFC stack. The performances simulated were much higher than the experimental values. This was probably due to some simplifications assumed on model development namely the unrealistic consideration of null methanol crossover. Zhang et al. [20] developed a thermal model to estimate thermal behavior of a MicroDMFC. The heat generation

by electrochemical reactions and by the heater was considered. The thermal loss that influences negatively the maintenance of an optimal temperature was also studied. The heat taken away by the methanol solution, thermal convection, radiation, and heat emission were considered as main thermal loss components. Some simplifications were made, namely, steady state condition and negligible temperature gradients inside the cell. A set of 3D simulations was conducted using ANSYS that employs Finite element analysis (FEA). Different patterns of the heater were simulated and compared to optimize heating effect. The simulation results showed that the heaters applied by a current generate heat to increase the operating temperature with different temperature distributions. Ghayor et al. [34] developed a 3D, steady flow, multi component, non-isothermal and single-phase model. The flow in the channels was characterized by using the CFD code FLUENT, simulating dropping pressure, velocity and heat transfer of the cell. The model was used to investigate the velocity contours of two designs (cross-strip and parallel). CFD was also used to investigate the effects of flow field structures on a MicroDMFC performance by Wang et al. [23] using a 3D anodic numerical model. FLUENT was used to simulate the effects of flow field structure on temperature distribution and flow velocity distribution. Four different types of flow fields including double serpentine, parallel, helix and single serpentine were simulated. The model included some simplifications: methanol crossover was ignored, steady state conditions were assumed and the phase change and thermodynamic equilibrium effects on two-phase flow were not considered in the channels. The authors only focused on the simulation of fluidic flow and heat transfer in the anode. From the four designs studied the double-serpentine anodic flow field generated higher power densities at a proper velocity. A cathode 3D two-phase mathematical model was developed by Zhang et al. [31]. Some simplifications were made, i.e., steady state and isothermal conditions were considered and the water vapor was neglected in the cathode. The coupled equations were numerically solved using COMSOL Multiphysics 3.6. Compared with the conventional cathode perforated structure, the simulation results indicated that the perforated structure with parallel flow channels presented could enhance the oxygen mass transport and reduce the water flooding to improve the cell performance.

Modeling and simulation studies are relatively scarce on MicroDMFC area. There are some references reporting 2D models and 3D CFD simulations but more work is still needed in this field. The development of a one-dimensional model, including thermal effects could be very useful for quick predictions. Special attention should be devoted to the inclusion of methanol crossover because it affects negatively fuel cell performance. Also, transient simulations should be also implemented.

4. Conclusions

In the last years, many efforts have been made in the development of MicroDMFCs to enhance their performance. In this work the recent technical developments in MicroDMFCs are summarized. Many studies have focused on analysis and improvement of single parts of MicroDMFCs systems and different materials, designs and operating conditions have been suggested. Although the results of these studies are useful, it is important to note that materials and conditions optimized for one type of MicroDMFC may be not always recommended for another. This is because MicroDMFCs systems engage different physical and chemical coupled processes; in this way, when developing a MicroDMFC, the materials and conditions need to be carefully chosen in order to achieve optimal performance or power output. Regarding the operation conditions, for an existing MicroDMFC it is possible to enhance performance using different methanol concentrations, flow rates and temperatures. As presented in this work, it is also possible to increase power output using different flow field designs and fuel and oxidant delivery systems. A great challenge on the development of this type of fuel cell, in order to be used in real applications, is the development of cost-effective materials. To achieve that, different materials have been, recently, explored as current collectors, membrane, and diffusion and catalyst layers both for the anode and cathode side, as well as, different microfabrication techniques achieving improved power generation. However, additional studies on more cost-efficient electrode materials and optimization of configurations are needed. Another key factor when a micro-fuel cell is projected is the fuel cell design (conventional or planar). For some applications, the simplicity of planar design could be crucial. However, fuel cell performances are yet limited.

Since the MicroDMFC systems involves electrochemical processes, energy, mass and charge transfer, a better understanding of the basic transport phenomena is essential to achieve the energy densities needed for real applications. Mathematical models appear as a useful tool to understand and predict the main transport phenomena and electrochemical processes helping in MicroDMFC optimization in terms of design and power output. Different approaches are available in literature regarding the MicroDMFC modeling, although only a few models describe all the internal phenomena processes. These models can be used to investigate the effects of various operating and structural parameters on cell performance, however more complex models, like CDF models, involve extensive calculations with higher computing times, making their practical usefulness relatively low. To avoid that it is necessary to developed analytical and semi-empirical models (using applied mathematical techniques and computing power) to obtain useful, reduced models, which can be used to understand and predicts the effect of the basic variables on power output. Such models are helpful for the discovery of new cell designs and operation regimes of the MicroDMFC systems.

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